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HYPERSENSITIZING COMMERCIAL PANCHROMATIC
PLATES

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Introduction

Ordinary dry plates, which owe their sensitivity to the silver halides alone, are sensitive only to the violet and blue regions of the spectrum. If, however, a suitable dyestuff be added the emulsion becomes sensitive to other regions, the particular region depending on the dye used. Thus erythrosin sensitizes to the green and greenish yellow, pinaverdol to the green and yellow, pinacyanol to the orange and red and dicyanin to the extreme red and infra-red.

The dyestuff is applied to the halides in one of two ways. In the commercial orthochromatic (sensitive to green and yellow) and panchromatic (sensitive to all colors) plates, the dyes are incorporated in the emulsion and the mixture flowed over the glass plate. The second method consists of bathing an ordinary blue-sensitive plate in a dilute solution of the dye and allowing the plate to dry.*

*Eder, Handbuch der Photographie 1902, Vol. III, page 169 et seq. For the Bureau of Standards methods see Bulletin Bureau of Standards, 14, 371, 1917

The bathed plates are in general faster than the commercial plates* and of course have the advantage that the

*Eder Handbuch der Photographie 1902, Vol. III, page 169 reference to Schumann Oct. 1885, Phot. Wochenbl. 1885 page 395.

plates can be sensitized for any desired region. Certain

dyes, moreover, (dicyanin for example) can not be successfully incorporated in the emulsion. The bathed plates, however, if not used soon after bathing, or if kept at a high temperature, are, in the case of most dyes, more susceptible to chemical fog. Dicyanin and pinacyanol bathed plates when prepared so as to produce the greatest sensitivity are useless after three or four days.

It has long been known that, though at the expense of keeping qualities and freedom from chemical fog, the speed of bathed plates can be increased by the addition of ammonia to the dye-bath. Since this increase is quite marked in the case of some dyes, it was hoped that in this way commercial plates could have their speed increased and at the suggestion of Dr. P. W. Merrill, a study was made at the Bureau of Standards of the influence of ammonia on commercial orthochromatic and panchromatic plates.

Sensitometry

Three methods of sensitometry were used: first the three color screen method, second the spectrograph method and third the Hurter and Driffield method.

The first method based on Abney's method*, which, however,

*Phot. Jour. June 1895.

Eder, Photo Korr. 1903, p. 426.

Chapman Jones, Photo. Jour. 1901, 256.

was used only as a qualitative method at first, consists of exposing the plates to a constant light source (usually a nitrogen filled tungsten lamp corrected by color screens so as to have an energy distribution similar to daylight) behind a so-called trichromatic sensitometer plate. This plate is a neutral screen having four strips of squares of increasing density, each square having twice the density of the preceding. One of these strips is left white while on the others are placed a red, a green and a blue filter intended to be of the same luminosity and complementary. The plates to be tested are thus exposed to varying intensities of white, red, green and blue light.

The second method avoids the difficulty of obtaining filters transmitting pure spectral colors, by exposing the plate in a spectrograph.

The apparatus, Fig. 1, consists of a concave grating of 50 cm. radius with 20000 lines per inch, mounted in parallel light with a 100 watt "daylight" tungsten lamp on 110 volt A.C. circuit as a source. For use with color sensitive plates a piece of yellow glass (7 mm. thick, Corning G 361 CE) barely transmitting the hydrogen blue line with wave length 4861 A was placed in front of the slit to cut out the second order blue. The region photographed was from about 4900 A to the limit of sensitivity of the plate. A pair of cross

Fig. 1

- a. Lamp source
- b. Yellow glass screen
- c. Slit
- d. Concave mirror
- e. Concave grating
- f. Photographic plate to be tested

hairs just in front of the plate at the position of the red line of hydrogen (wave length 6563 A) and of the blue line (4861 A) served as reference marks. Fig. 2 gives the energy distribution of the lamp and screen combination. The energy was determined in the spectrophotometric laboratory, visually on a König-Martens Spectrophotometer, by a substitution method of comparison with a radiometrically calibrated Mazda lamp.

The photographic densities were measured on a Hartmann Microphotometer. This method gives immediately the sensitivity of the plate to all parts of the spectrum; but since, during the course of the work minor changes (change of slit, resilvering of mirror, etc) were made, the exposure times on different sets of plates were not always equivalent.

Furthermore, since the plates were of different kinds and showed markedly different rates of development, they were in this part of the work, developed by tray until they showed the amount of fog allowable in plates to be used in general photography. The density of the silver deposit obtained depends on the time of development, so that in the curves obtained the shapes (maxima and minima) are the really important parts and the density is only approximately a measure of the speed.

Fig 2

The method generally adopted for the measurement of the speed is that of Hurter and Driffield*. Specimens of

*Hurter and Driffield, Jour. Soc. Chem. Industry May 1890, p. 455.

the plate to be tested are exposed for the same time, behind a sector wheel, to a standard light source. The transmission T of the images obtained are measured and their densities, defined as $-\log T$, are plotted as ordinates and the logarithm of the time of exposure E as abscissas.

The curve so obtained is known as the characteristic curve of the plate. It consists of three parts, the first part is concave upward, the second is a straight line and the third is concave downward. Project the straight line part of the curve until it intersects the axis of abscissas. The numerical value of the exposure at the point of intersection is known as the inertia i of the plate and the speed is defined as $\frac{1}{i}$. Hurter and Driffield showed that this inertia of a plate is independent of the kind of developer used (except for strong pyro and for the presence of free bromide) and of the time of development. See Figs. 3 and 4. Free bromides, either in the film or in the developer, shift the point of intersection of the straight line portions of the curve to a point below the axis. See Fig. 5.

The Hurter and Driffield speeds for several ammoniated and unammoniated plates were obtained, using an apparatus

2.00

1.00

-2.00

Ilford Special Rapid Panchromatic (5650K)
Treated
No filter

Speed 18.2

Minutes (time of development)

3 minutes

1 minute

Fig. 3 Log E

+1.00

2 00

Ilford Special Rapid Panchromatic (5630N)

Untreated

No filter

Speed 4.45

Density

1 00

-2 00

Cramer Spectrum Process (1439)

Treated

Wratten "F" Filter

Speed 1.88

2.00

Cramer Spectrum Process (1439)

Untreated

Wratten "F" filter

Speed 0.49

-0.01

Density

Fig. 6

2.00

Cramer Spectrum Process (1499)

Treated

No filter

Speed 25.1

-2.00

-1.00

0.00

+1.00

Fig. 7

2.00

Cramer Spectrum Process (499)

Untreated

No filter

Speed 10.2

Log E

Fig. 8

Eastman E IV^d
Treated
Wratten "F" filter

Speed 2.18

Density

2.00 -

61

Fig. 9

2.00

Eastman EIV^d
 Untreated
 Wratten "F" filter

Speed 0.57

Density
 1.00

-1.00

Fig. 10

Eastman E IV^a

Treated

No filter

Speed 17.7

Fig. 11

2.00

Eastman E IV^a
 Untreated
 No filter

Speed 12.6

Density

0.00
 -2.00

1.00

Fig. 12

designed and built by Mr. R. Davis of the Bureau of Standards. The light source (a calibrated tungsten lamp) is corrected for daylight, and means are provided for accurately controlling the current through the lamp, the speed of the sectored disc and the total time of exposure. See Figs 3 to 12 inclusive.

Procedure

A series of Cramer Spectrum Process and Ilford Special rapid Panchromatic plates were bathed for four minutes at 16° to 18°C in water containing increasing amounts of ammonia, and were then exposed in the spectrograph. Both Metol-Hydroquinone and Pyro developers were used. It was soon found that the plates showed fog in development unless they were kept cool while drying and were dried rapidly. The plates showed a progressive increase in speed with increase in ammonia concentration until, with a bath containing 4 cc. of ammonia water (containing 20% NH_3) in 100 cc. distilled water, the plates began to fog so badly in development as to be useless.

The ammonia was then added to water-alcohol mixtures of varying concentration. The plates bathed in the alcoholic ammonia did not have their sensitivity increased as much as in the corresponding water baths, but were very much cleaner working. Seventy-five parts of water to twenty-five of

ethyl alcohol gave the best results, and this proportion was adhered to thereafter. Sometimes the plates showed a slight network of fog (mottling) similar to the drying marks shown when plates are dipped (not soaked) in alcohol to hasten drying. Washing in 95% alcohol for 20 or 30 seconds after the ammonia bath prevented this, but this final wash is not usually necessary, especially if the plates are not forced in development.

Fig. 13 gives the spectral sensitivity curves of a series of Cramer Spectrum Process plates in baths containing 1/40, 1/10, 1/2, 1 and 3 cubic centimeters of 20% NH_3 to an alcohol-water mixture of 25 parts of alcohol and 75 parts of water.

Three to three and one-half cubic centimeters of the strong ammonia to 75 cc of water and 25 cc alcohol was adopted as the combination to be used, and, except for a few trials on various plates, the plates were all treated with this same mixture.

The time of bathing, 2, 4, or 6 minutes, had no appreciable effect, provided that the film was bathed long enough to get thoroughly soaked. Four minutes was the time used for bathing in all subsequent experiments.

For a study of the keeping qualities of the plates, a number of Cramer Spectrum Process and Ilford Panchromatic

Cramer Spectrum Process (1439)

a	Untreated	(BX 142)
b	1/40 cc ammonia	(BX 173)
c	1/10 cc "	(BX 175)
d	1/2 cc "	(BX 177)
e	1 cc "	(BX 178)
f	3 cc "	(BX 180)

to

75 cc water
25 cc alcohol.

Same exposure
and development.

Fig. 13

plates were treated and samples of the treated plates exposed and developed after being stored for various lengths of time. The Cramer plates showed deterioration after a week but were still usable. The Ilford plates were useless after 3 or 4 days. The plates bathed without the use of alcohol deteriorated more rapidly.

The bath of 3 to $3\frac{1}{2}$ cc of ammonia water (20% NH_3), 25 cc of alcohol and 100 cc of water is recommended. Three and one-half cubic centimeters ammonia water to 100 cc of water is used where the maximum increase of sensitivity is desired, but the plates are much more susceptible to fog in development and must be used immediately after drying. Development should be carried out using the Wratten Safelight No. 3 and over-development carefully guarded against.

Ordinary Plates

As is well known, the speed of the silver halide emulsion can be increased by treatment before it is flowed on the plate. This treatment, known as "ripening" is usually either to keep the emulsion at a high temperature for some time or to add ammonia. This ripening by ammonia is effective even after the plates are ready for use*

*Eder, Handbuch III, p. 63.

On ripened plates such as the Seed 30 and Central

Special, and on the Seed 23, there is no appreciable increase in speed when they are bathed in ammonia. In some cases there is rather a slight decrease in speed. On one plate known to have been ripened by the ammonia process before coating, (Central Dry Plate Co.) which, however, was not fresh, this increase in speed on subsequent bathing in ammonia was quite apparent.

Microscopic examination of the treated and untreated plates showed no difference in the size of the grain.

Orthochromatic Plates

A number of plates sensitive to the green and yellow were tried. Most of them showed no appreciable change in sensitivity. Some had the sensitivity decreased, e.g. Cramer Commercial Isonon. The sensitivity of the Seed Aero Ortho was increased slightly.

Fig. 14 is a print from treated and untreated Cramer Commercial Isonon negatives obtained through the tricolor sensitometer plate. Fig. 15 is a similar set on the Seed Aero Ortho. It will be noted that the change in sensitivity can be observed in all the strips.

The Cramer "Trichromatic" showed an increase in sensitivity comparable to that observed in the Spectrum Process.

Treatment of Eastman and of Ansco N.C. films, which are orthochromatic, showed no change larger than the differences attributable to experimental errors.

Fig. 14

Fig. 15

Panchromatic Plates

Every panchromatic plate tried showed remarkable increase in speed. The very fast plates, several of which were developed only recently in response to the need for fast color sensitive plates for aerial photography, showed a somewhat smaller increase than the slower and process plates.

The plates examined were:

Cramer Spectrum Process	
Ilford Panchromatic (Special Rapid)	
Five of the Eastman Special Experimental Panchromatic plates	
Wratten and Wainwright Special Red Sensitive	
" " " R.F.C. Panchromatic	
" " " Panchromatic	
Wratten M	
Cramer Spectrum #11	
Cramer G D I, G D II, G D III	
Central Experimental Panchromatic	

Wherever possible several different emulsions were used.

Figs. 16, 17, and 18 are prints from pairs of Wratten and Wainwright Special Red Sensitive, one of the Eastman Experimental emulsions and Ilford Panchromatic plates. The three sets of prints were exposed and developed exactly alike on Artura Iris paper. Even though the paper cannot reproduce all the gradations of the original negative, they do give fairly well the relative speeds of these three brands of plates and show quite well the great increase in speed effected by the ammonia treatment.

This sensitometer plate method gives the relative speeds

Untreated Ilford Pan (56418) Treated
Special Rapid.

Fig. 18

Fig 19

of plates towards filters, but since the filters do not transmit pure spectral colors (the blue transmits a band in the red and the transmission of the three filters overlap) more can be learned of the color sensitivity from the spectrograph curves.

Fig. 19, a print from a treated and an untreated Spectrum Process Plate, shows the sensitivity of the plate to each wave length.

Fig. 20 gives the spectral sensitivity curves obtained with the Spectrum Process plate: 5 and 10 second exposures on the treated and 10 seconds exposure on the untreated plate.

Fig. 21 gives the curves for one of the Eastman Kodak Co.'s special experimental Panchromatic Plates, both for 10 second exposures.

In Fig. 22, curve a is for the 10 second exposure on the untreated Ilford Panchromatic plate. Curve b is for the 5 second exposure on the treated plate.

One of the most striking changes produced by the ammonia treatment was the action on old panchromatic plates. A Wratten and Wainwright plate marked "use before Sept. 15, 1915", was exposed* in the spectrograph. As was to be expected, the plate was badly fogged on the edges and the sensitivity of the emulsion was much below that of a fresh plate. Treatment with ammonia brought the sensitivity up to an even

* October 21, 1918

Cramer Spectrum Process (1439)

- a Untreated 10 second exposure (BK54)
- b Treated 5 second exposure (BK53)
- c Treated 10 second exposure (BK53)

Fig. 20

Eastman Special Experimental Panchromatic (E II & 2165 D)

a Untreated (BX 36) 10 sec
b Treated (BX 32) 10 sec

Ilford Special Rapid Panchromatic (56418)

a Untreated 10 second exposure (BK121)
 b Treated 5 second exposure (BK120)

Fig. 22

greater value than that possessed by a fresh plate. See Figs. 23 and 24.

The Hurter and Driffield curves for some of these plates gave the following values for the speed:

	Untreated	Treated
	White Light	
Cramer Spectrum Process (1439)	10.2	25.1
Eastman Experimental Panchromatic IV d	12.6	17.7
Ilford Special Rapid Panchromatic (5630N)	4.45	18.2
	Minus Blue Filter	
Eastman Experimental Panchromatic 2199	1.91	4.37
Ilford Special Rapid Panchromatic (56416)	4.37	13.5
Standard Orthonon	23.	
	F Filter	
Cramer Spectrum Process (1439)	0.49	1.88
Eastman Experimental Panchromatic IV d	0.57	2.18

The figures give the absolute speeds of the plates to white light and through the Wratten Minus Blue and F filters on the Hurter and Driffield scale. The value for the speed of the Standard Orthonon plate through the Minus Blue filter obtained on the same apparatus is given for comparison. The Minus Blue, a deep yellow filter, cuts out all the blue and violet light while the F, a deep red, transmits only the long red wave lengths.

Fig 23

Wratten & Mainwright Panchromatic (935)

Expiration date Sept. 1915

Used Oct. 1918

- a Untreated 10 sec. exposure (BK 91)
- b Untreated 20 " " (BK 91)
- c Treated 10 " " (BK 90)

These figures show the remarkable increase in speed of the plates, particularly in the long wave length region. Thus the Cramer Spectrum Process plates are increased in speed 150% to white light and nearly 400% to the red. Through the Minus Blue filter, one of the Ilford plates is increased 300%.

These plates were used in experiments in airplane photography, where, for photographing through the haze, a fast red-sensitive plate is necessary. Fig. 25 is a set of prints from the Ilford plates. Prints a and b were printed for the same time from the untreated and treated plates. Print c is from the untreated negative, timed to give the best print. The negatives were given the same exposure in the air and were exposed within a few seconds of each other, through the Minus Blue filter.

The increased speed of the treated plate is apparent. It will be seen also that the treated plate is less contrasty and gives much better detail in the shadows.

Fig. 26a is from a treated Cramer Spectrum Process plate used with the Minus Blue filter and b is from a similar plate with the F filter. The increased haze penetration obtainable by the use of the red filter is clearly shown.

a (Untreated)

Ilford Special Rapid Panchromatic Plates
Minus. Blue Filter

c (Untreated - same negative as a)

a) printed 24sec.

c " 8sec

Fig. 25

b (Treated)

a

Treated Cramer Spectrum Process - Minus Blue
Filter

b.

Treated Spectrum Process F filter

Fig. 26

Action on Minima

On every plate which had an irregular curve of spectral sensitivity, the minima were raised and in many cases smoothed out entirely. For example, note the minima at 6100 A, Fig. 20, at 5150 A and 6190 A, Fig. 21 and at 5150 A and 6100 A, Fig. 24. This property of the ammonia treatment adds greatly to the value of the plates in the photography of spectra especially as the sensitivity is extended some 200 Angstrom units further into the red at the same time. The bad effect of a minimum is, however, smoothed out to some extent in ordinary photography through filters.

Plates With Known Dyestuff

The difference in behavior between the ordinary and orthochromatic plates and the panchromatic plates shows clearly that the sensitivity increase dealt with here is not that observed by Eder, which is due to "ripening" but is an action associated with the dyestuff.

The effect of the ammonia is to increase the sensitivity of the emulsion to the incident light and not to increase the developability of a latent image already formed, since a plate treated with ammonia after exposure but before development showed no increase in sensitivity. That the

action is not due to the alkalinity of the bath is shown by the fact that bathing in a solution of sodium hydroxide having the same concentration of OH ions had no effect on the speed of the plate.

Part of the increase in speed is, probably, due to the fact that some of the dyestuff in the gelatine film is washed out and its screening effect diminished. The ammonia bath becomes colored with use and a color difference is observed between the untreated and treated plate before development.

The pinaverdol dyes sensitize for the green and yellow and any orthochromatic plate containing one of this series of dyes have the sensitivity increased by the ammonia treatment. Fig. 27 is a plate made up by the Cramer Dry Plate Co., using Pv I₂ pinaverdol made by the Bureau of Chemistry, and marked by Cramer "similar to Trichromatic". The Trichromatic plate has the sensitivity curve of a pinaverdol dyed plate and Fig. 28 gives the curve before and after ammonia treatment.

Mixtures of pinaverdol and pinacyanol are the dyes usually used in the preparation of panchromatic plates intended for spectrum photography. The mixtures of these two dyes alone leaves a strong minimum at about 6100 Å. The ammonia treatment smooths out the minimum. In many plates

GD IV R₁L₂ (Similar to Trichromatic)

a Untreated 10 sec. exposure (BK 191)
 b Treated " 10 sec. (BK 192)

Fig. 27

Cramer Trichromatic #21

a Untreated 10 sec exposure (BK183)
 b Treated 10 " " (BK184)

Fig. 28

intended for general photography other dyes are added to sensitize in this region. See Fig. 24.

Fig. 29 gives curves for a plate (similar to their Spectrum Plate) made up by the Cramer Co. using a mixture of the Bureau of Chemistry's Pc XII pinacyanol and Pv I₂ pinaverdol. It will be noted that the addition of pinacyanol lowers the maximum due to the pinaverdol. Fig. 30 is a similar plate with more pinaverdol. The plate given in Fig. 31 was made up with Pc IX, another of the pinacyanol series.

The dyes used in sensitizing are nearly all basic dyes and it is not probable that the ammonia changes the dye itself. On the addition of ammonia to the dye solution before bathing there is no color change. It is possible that the solvent action of the ammonia on the silver halide facilitates the reaction between the dyestuff and the silver salt, in addition to its softening effect on the gelatin. This, however, does not account for the raising of the minima. It is possible that there is the formation of a $\text{AgNH}_3\text{Cl} + \text{Dyestuff molecule}$, with a photosensitiveness slightly different from that of the original molecule.

GD III P_{XII} and P_{VI} (

a Untreated 10 sec. exposure (BK 189)
 b Treated 10 " " (BK 190)

Fig. 29

GD II Fe XII and PvI_2

a Untreated 10 sec. exposure (BK 187)
 b Treated 10 " " (BK 188)

GDI P_{eIX} and P_{vI_2}

a Untreated 10 sec. exposure (BX/15)
 b Treated 10 " " (BX/100)

Fig. 31

Summary

Since ammonia, when added to the dye bath in preparing bathed plates, increased the sensitizing action of the dye, its action on commercial plates was investigated.

In the course of the work three methods of sensitometry were used. Of these, one was used as a first qualitative test, the second, the spectrograph method, was used to study the effect of the ammonia on the sensitivity of the plate to each wave length. The third, the Hurter and Driffield method, gives the absolute value of the speed of the plate.

It was found that by bathing commercial panchromatic plates in a solution of 25 cc ethyl alcohol, 75 cc water and 3 cc of strong ammonia water (20% NH_3) for four minutes and drying, the speed to white light is increased 100% in nearly all cases, and the sensitivity in the red extended one hundred or more Angstrom units. The speed in the red is increased, in many cases, 400%. If the plates be bathed without the alcohol (100 cc water, $3\frac{1}{2}$ cc ammonia water) the speed is still more increased but the plates should be used immediately after drying.

Ordinary plates do not have their sensitivity appreciably changed. Most brands of orthochromatic plates are not improved although one, the Cramer Trichromatic, showed the same increase as the panchromatic plate.

My thanks are due to Dr. J. S. Ames for his supervision of the present investigation and for valuable advice rendered during many conferences.

The energy distribution of the light source in the spectrograph was determined by Mr. E.P.T. Tyndall and Mr. H.J. McNicholas of the spectrophotometric laboratory. I am also indebted to Mr. R. Davis and Mr. F. M. Walters, through whose help the Hurter and Driffield curves were obtained and to Dr. C. C. Kiess under whose direction and cooperation most of the work was done.

May 26, 1919

Biographical Sketch

Samuel Moses Burka, son of Meyer and Ida (Zinberg) Burka, was born May 26, 1891 in Union Springs, Ala. He entered the undergraduate department of the Johns Hopkins University from the Baltimore City College in 1909. He received the baccalaureate degree in 1913 and entered the Chemistry Department of the graduate school, attending lectures by Professors Morse, Jones, Acree and Lovelace. In 1914 he entered the Physics Department, taking Physics, Physical Chemistry and Astronomy, attending lectures by Professors Ames, Wood and Pfund in Physics, Professor Anderson in Astronomy, and Professor Cohen in Mathematics. He received the degree of Master of Arts in Physics in 1916, the title of his essay being "Radioactive Atoms".

During the years 1913-1914 and 1914-1915 he held Hopkins Scholarships. In the summers of 1910, 1911 and 1912 he was assistant to Professor Gilpin in the Summer School. During the years 1911-1912 and 1912-1913 he was Student Assistant in Chemistry, and during 1915-1916 and 1916-1917 was Student Assistant in Physics and Lecture Assistant to Professor Ames. In the spring of 1917, under leave of absence from the University, he received an appointment as Laboratory Assistant in the Spectroscopy Section of the Bureau of Standards, and in February 1918 was promoted to Assistant Physicist.